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FEASIBILITY OF LIQUID ION EXCHANGE FOR EXTRACTING PHOSHATE FROM WASTEWATER

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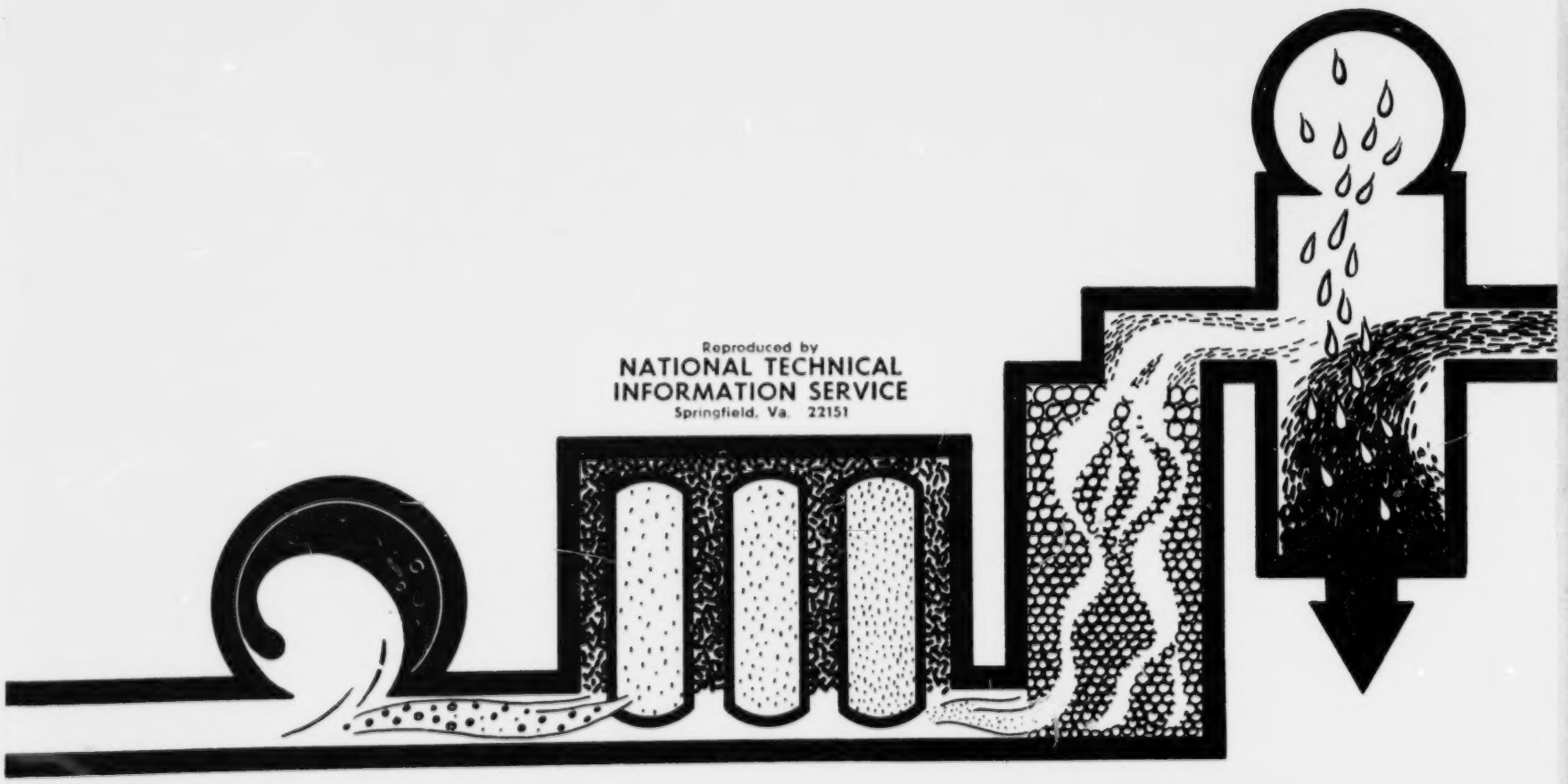

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16. Abstract The liquid ion exchange extraction process has been used consistently for removing small quantities of uranium, vanadium, copper and other metals. In successful tests of the ability of liquid ion exchange to remove ABS from sewage plant effluents, it was discovered that some phosphorus was removed also. Various metal-containing organic compounds were screened for their activity as liquid ion exchange reagents for phosphate. The compounds were tested for selectivity in extracting inorganic phosphate from water into organic solvents in the presence of chloride, sulfate, and bicarbonate. A tribenzyltin hydroxide, with a component identification as containing tribenzyltin carbonate and a tribenzyltin carboxylic acid salt, extracted 52% of phosphate from an aqueous solution containing 25 mg/l phosphate, 166 mg/l chloride, and 212 mg/l sulfate at pH 4.1. A tribenzyltin acetate compound was also successful in extracting phosphate but the extraction was not as complete as with the tribenzyltin hydroxide compounds. Tribenzyltin benzoate, triphenyltin hydroxide and several others, as well as trivalent iron, aluminum and chromium salts of di-2-ethylhexylphosphoric acid did not exhibit any significant phosphate extracting activity. (Lowry-Texas)

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FEASIBILITY OF LIQUID ION EXCHANGE

FOR EXTRACTING PHOSPHATE FROM WASTEWATER

by

General Mills Chemicals, Incorporated
Minneapolis, Minnesota 55434

for the

ENVIRONMENTAL PROTECTION AGENCY

Program #17010 EAP
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ABSTRACT

A variety of organic compounds were screened for utility in extracting inorganic phosphate from water by the liquid ion exchange process.

Organometallic compounds, metal salts of di-2-ethylhexyl phosphoric acid and ferrocenium compounds were investigated. Only certain organometallics showed significant activity and this activity appeared to be concentrated in minor constituents present in the samples. More specifically, tribenzyltin compounds, possibly the hydroxide or its acid salts, were active in selectively extracting phosphate in the presence of chloride and sulfate.

This report was submitted in fulfillment of Program No. 17010 EAP, Contract No. 14-12-590, between the Federal Water Quality Administration and General Mills Chemicals, Incorporated.

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INTRODUCTION

THE REMOVAL OF PHOSPHATE FROM WATERS

Eutrophication of lakes by excessive algal growth has become a serious problem and has prompted considerable research on means for its prevention. One preventative measure that has special merit is the removal of phosphorus from municipal sewage plant effluents.

Secondary effluents from sewage plants contain substantial concentrations of phosphorus and constitute a major source of phosphorus nutrient for algal growth in natural waters. Of the various essential algal nutrients, phosphorus appears to be the one which might be most amenable to control. Therefore, the removal of phosphorus from sewage plant effluents could effect a phosphorus-starvation of the algae. It is believed that blooms of blue-green algae can be prevented by maintaining phosphorus levels of 0.01 mg/l in lakes (1).

Typical secondary effluents from municipal sewage plants contain approximately 8 mg/l phosphorus. Most of this phosphorus is in the orthophosphate form (2). Assuming that these effluents are diluted by a factor of 10 by the receiving body of natural water, a suitable treatment of effluent should reduce the phosphorus concentration to 0.1 mg/l. This would constitute a 99% phosphorus removal from an effluent containing 8 mg/l phosphorus.

A number of processes have been studied for removing phosphorus from sewage plant effluents. These include precipitation with chemicals, ion exchange, biological treatment, electro-chemical treatment, reverse osmosis, and electrodialysis. Precipitation and ion exchange appear to be most practical to date. Treatment with chemical precipitants, especially lime, is the most popular and most economical process. Precipitation with lime followed by filtration has been reported to effect approximately 95 percent phosphate removal at costs of at least 5 cents per 1000 gallons of water treated (3). Solid ion exchange with resins also has shown potential for removing phosphorus from sewage plant effluents. However, since the resins are not selective for phosphate, other anions are removed and therefore operating costs are estimated to be several times those for lime treatment (3).

Liquid ion exchange, a proven process for removing small quantities of ions from water, however has not been investigated for phosphate extraction. This relatively new unit process is used commercially for recovering uranium, vanadium, copper and other metals (4,5). Its feasibility for removing alkylbenzene sulfonate detergent from sewage plant effluents has been demonstrated (6). This system for extracting detergent also reduced substantially phosphate concentrations. To date, however, there has been no concerted study on the potential of liquid ion exchange for phosphate extraction.

Liquid ion exchange processing has certain features that make it attractive for the treatment of sewage plant effluent. It is a continuous hydraulic process, especially amenable to the treatment of large volumes of continuously flowing water. It has flexibility to accomodate for changes in the effluent and is readily automated. It is capable of concentrating extracted species at least one thousand-fold. Its economics are competitive with other established commercial processes such as precipitation and solid ion exchange. It is especially amenable to the incorporation of selectivity for one chemical species, e.g., phosphate.

The contamination of treated water with solvents might appear to be a deterent to the use of liquid ion exchange on sewage plant effluent. In commercial metal extraction by liquid ion exchange, approximately 150 mg/l of solvent are entrained in the treated water. But in these cases, contamination of the water is no problem and economics are satisfactory, therefore no effort is made to prevent this entrainment loss of solvent. With proper engineering of the process and proper choice of liquid ion exchange reagent, this contamination of the treated water probably could be reduced to the 1 mg/l level.

LIQUID ION EXCHANGE - PRINCIPLE

Liquid ion exchange is a relatively simple unit process for extracting ions from water. Figure 1, a flow diagram of a conventional liquid ion exchange plant, illustrates the principle involved.

In this diagram, water containing A^- the ion to be extracted flows into a mixer. Here it is contacted with the liquid ion exchanger, a solution containing several percent liquid ion exchange reagent in a high boiling hydrocarbon. The reagent is a water insoluble organic compound having functionalities that have an affinity for A^-. During this

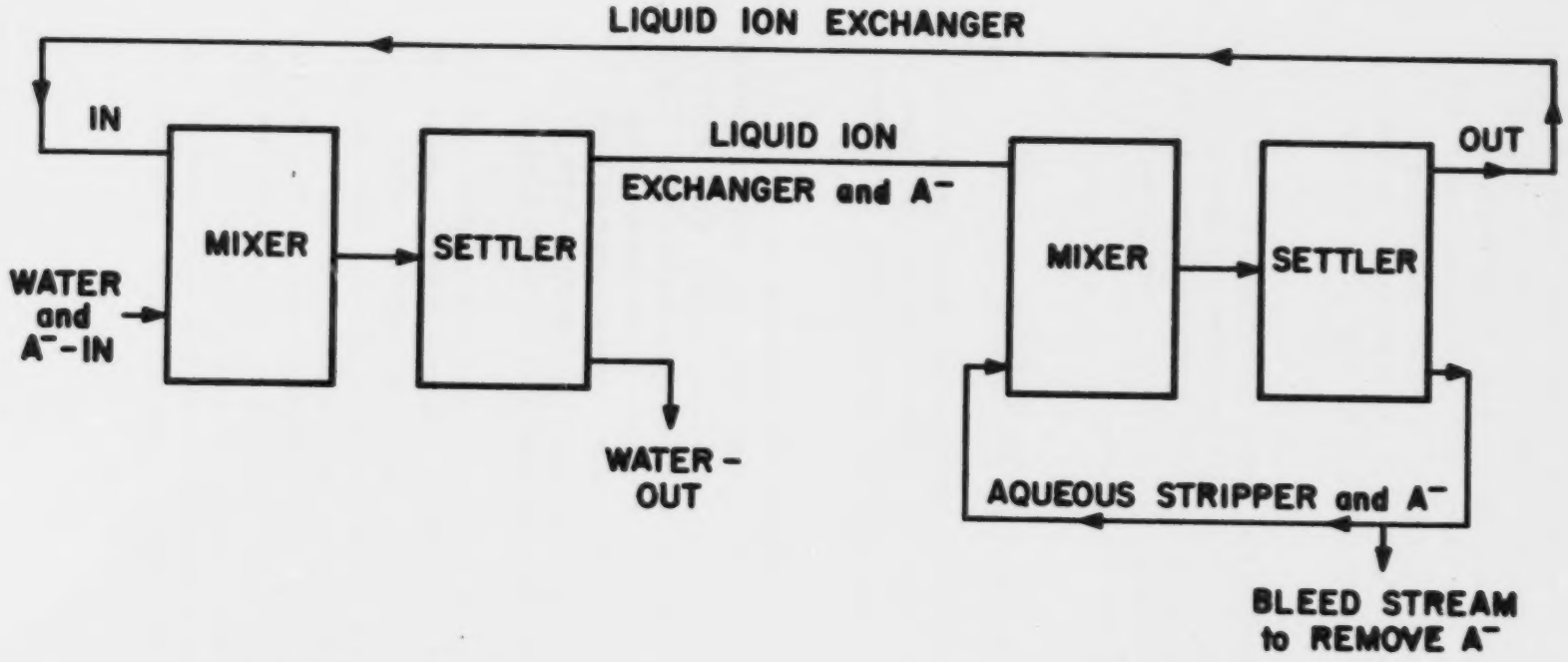


Figure I. Flow Diagram of Liquid Ion Exchange Plant

contact, A^- is extracted from the water into the liquid ion exchanger. The mixed liquids then flow into a settler. From here the treated water flows out the bottom and the liquid ion exchanger containing A^- flows out the top to the stripping stage.

In the stripping stage, A^- is stripped from the liquid ion exchanger by contact with an aqueous solution of a stripping reagent such as sodium hydroxide. The regenerated liquid ion exchanger from the settler is recycled back to the extraction stage to pick up more A^-. The aqueous stripping solution also is recycled for reuse with a portion bled off for continuous removal of A^- by precipitation or other means.

The liquid ion exchanger components have extremely low water solubility. The solvent is a hydrocarbon such as a high boiling kerosene. The liquid ion exchange reagent, is a high molecular organic compound having functionalities that combine selectively with A^-.

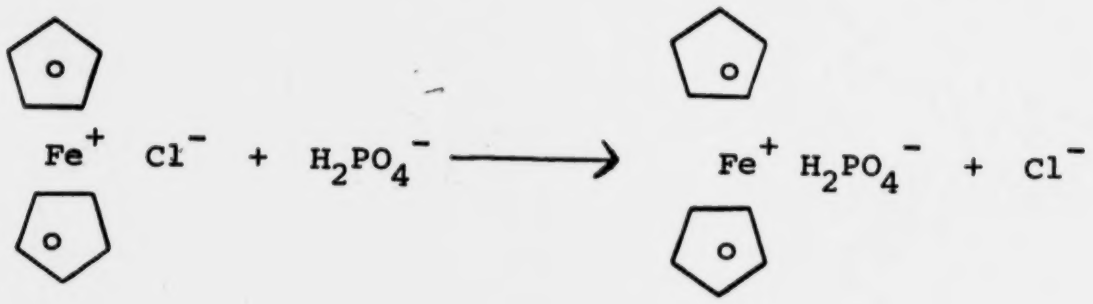
EXTRACTION OF PHOSPHATE BY LIQUID ION EXCHANGE

A literature survey (see Appendix) indicated that organic compounds containing metals would be good liquid ion exchange reagent candidates for selective phosphate extraction.

Organometallic compounds of the Group VA elements, e.g., As, Sb, Bi, and of Group IV A, e.g., Ge, Sn, Pb are reported as having affinity for phosphate. Also, Bock and Burhardt (7) and Schweitzer and McCarty (8) demonstrated that weak organometallic bases extract inorganic anions from water. Therefore, it appeared that weak organometallic bases of metals, e.g., organotin, organoantimony, etc. bases, should be investigated for phosphate extraction.

Another fruitful area for phosphate extraction appeared to be with metal salts of organic acids. Genge and Slamon (9) found that strong acid ion exchange resins loaded with trivalent metal ions reacted with phosphate. Thus, the metal salts of di-2-ethylhexyl phosphoric acids seemed to be likely candidates for complexing with phosphate. The trivalent salts of aluminum, iron and chromium appeared to be especially attractive. The desirable structures were $M(OH)_2O_2P(OR)_2$ where M is the trivalent metal ion and R is the 2-ethylhexyl group. It was anticipated that the OH ions would exchange for phosphate.

Ferrocenium compounds also were expected to have affinity for phosphate. For example, the following reaction was postulated.



Ferrocenium Chloride

The ferrocenium compound would have to be alkylated to provide the solubility in organic solvents that is needed by a liquid ion exchange reagent. The phosphate-loaded ferrocenium compound probably could be stripped of phosphate with a reducing agent such as sodium borohydride or sodium peroxide. This reduction, of course, would convert the ferrocenium compound to the ferrocene which would have to be reoxidized to the ferrocenium before reuse.

Generally, the experimental part of this study involved screening the above mentioned metal-containing organic compounds as liquid ion exchange reagents for selective phosphate extraction. Representative compounds were prepared and dissolved in an organic solvent. These organic solutions then were shaken with aqueous phosphate solutions containing chloride, sulfate and bicarbonate. The resulting aqueous solutions were analyzed to determine the extent of phosphate extraction and the selectivity of extraction.

AMMONIA EXTRACTION

The scope of contract No. 14-12-590 was changed at the request of the FWPCA after approximately eight months of investigation on phosphate extraction. The new direction was to investigate the feasibility of liquid ion exchange for extracting ammonia from water. About one month of effort was expended on the ammonia extraction study before the contract was terminated. See the addendum for more details.

SUMMARY AND CONCLUSIONS

Various metal-containing organic compounds were screened for activity as liquid ion exchange reagents for phosphate. The compounds were tested for selectivity in extracting inorganic phosphate from water into organic solvents in the presence of chloride, sulfate and bicarbonate.

A commercial tribenzyltin hydroxide contained a component which selectively extracted phosphate. The component was identified as containing tribenzyltin carbonate and a tribenzyltin carboxylic acid salt. A concentrate of this component extracted 52 percent of the phosphate from an aqueous solution containing 25 mg/l phosphate, 166 mg/l chloride and 212 mg/l sulfate at pH 4.1. No chloride or sulfate was extracted. An attempt to prepare a concentrate of the tribenzyltin carbonate was unsuccessful.

A commercial tribenzyltin acetate also selectively extracted phosphate in the presence of chloride and sulfate. The extraction was not as complete as with the tribenzyltin hydroxide component above and was not selective over bicarbonate. The phosphate extracting activity in this case also appeared to be due to a minor component.

Tribenzyltin benzoate, triphenyltin hydroxide, tri-n-butyltin hydroxide, triphenylantimony hydroxide, triphenyllead hydroxide and triphenylarsenic hydroxide did not show significant promise for use in extracting phosphate from water.

The trivalent iron, aluminum and chromium salts of di-2-ethylhexyl phosphoric acid did not exhibit any significant activity for extracting phosphate.

Alkylated ferrocenium compounds were prepared, but were too unstable for testing their phosphate extraction activity.

EXPERIMENTAL

EXTRACTION OF PHOSPHATES BY ORGANOMETALLICS

As mentioned earlier, our literature survey indicated weak organometallic bases will extract phosphates. Probable mechanism of extraction was as follows:

$$R_3MA + H_2PO_4^- \rightleftharpoons R_3MH_2PO_4 + A^-$$

Organometallic hydroxide compounds are good candidates for extracting phosphate. They are preferred over other organometallic anion compounds since the exchanging hydroxyl anion is not usually considered a pollutant of water.

The following organometallic compounds were tested for extraction of phosphate: tribenzyltin hydroxide, triphenyltin hydroxide, tri-n-butyltin hydroxide, triphenylantimony hydroxide, triphenyllead hydroxide and triphenylarsenic hydroxide.

Tribenzyltin Hydroxide

The extraction of phosphate by tribenzyltin hydroxide ($[C_7H_7]_3SnOH$) was studied at pH 8.3, 7.0 and 4.1. Utilization of this wide pH range enables one to identify compounds which are selective for phosphate both at low and at high pH's. If a compound was found to be selective for phosphate at pH 4, modification of the organic structure could raise the effective extraction pH to perhaps 7 or 8. The latter pH's are more realistic in waste water systems. The compositions of the aqueous phosphate stock solutions used in the extraction studies are shown in Table I.

Extraction studies were performed as follows: an organic solution of the organometallic compound was prepared in toluene so that 5 ml contained two times as many equivalents of organometallic as $H_2PO_4^-$ equivalents in 100 ml of the aqueous stock solution. Five ml of a 4.3 g/l solution of tribenzyltin hydroxide (Alpha Inorganics lot no. 12268) and 100 ml of aqueous stock solution were shaken together for 2 minutes in a separatory funnel. The phases were allowed to separate. The aqueous layer was drawn off, filter-

ed and analyzed. The above procedure was repeated using 25 ml of tribenzyltin hydroxide solution. A summary of the extraction data is shown in Table II.

TABLE I. COMPOSITION OF AQUEOUS PHOSPHATE STOCK SOLUTIONS*

Solution	A	B	C	Analytical Procedure References
pH	8.3	7.0	4.1	
$PO_4^{\equiv}$	24.1	23.6	24.8	Standard Method**
$SO_4^{=}$	213	254	212	ASTM D516
Cl^-	158	142	166	Standard Method**
HCO_3^-	336	286	---	ASTM D513

* All concentrations are in mg/l

** "Standard Methods for the Examination of Water and Wastewater", 11th ed.

TABLE II. EXTRACTION OF PHOSPHATE WITH TRIBENZYLTIN HYDROXIDE

Expt	Volume Ratio, org/aq	pH initial	pH final	[Phosphate] i., mg/l	[Phosphate] f., mg/l	% Phosphate Extracted
1	5/100	8.30	8.48	24.1	24.3	0
2	25/100	8.30	8.50	24.1	23.8	0
3	5/100	7.00	7.82	23.6	24.3	0
4	25/100	7.00	8.00	23.6	24.8	0
5	5/100	4.10	6.27	24.8	22.4	9.7
6	25/100	4.10	6.90	24.8	17.3	30.3

Further analyses of the raffinate from the experiment at pH 4.1 (5 & 6) indicate no extraction of sulfate or chloride. Thus, at pH 4.1 the tribenzyltin hydroxide selectively extracted phosphate in presence of chloride and sulfate.

Tribenzyltin hydroxide (Lot #12268) from Alpha Inorganics was examined by infrared spectroscopy. The infrared spectra was quite weak in OH absorption. Thus, it was questionable as to how much of the sample was really tribenzyltin hydroxide. Furthermore, the melting point of the sample was 110-120° C, whereas literature reports 117-121° C (10).

The tribenzyltin hydroxide (Lot #12268) was crystallized from toluene to determine if the phosphate activity could be concentrated. One crystallization gave 57% by weight clear triclinic type crystals (Fraction A). These crystals when dissolved in toluene did not extract any phosphate from the pH 4.1 phosphate solution. Both extraction experiments were carried out using the same weight concentration of organic in toluene.

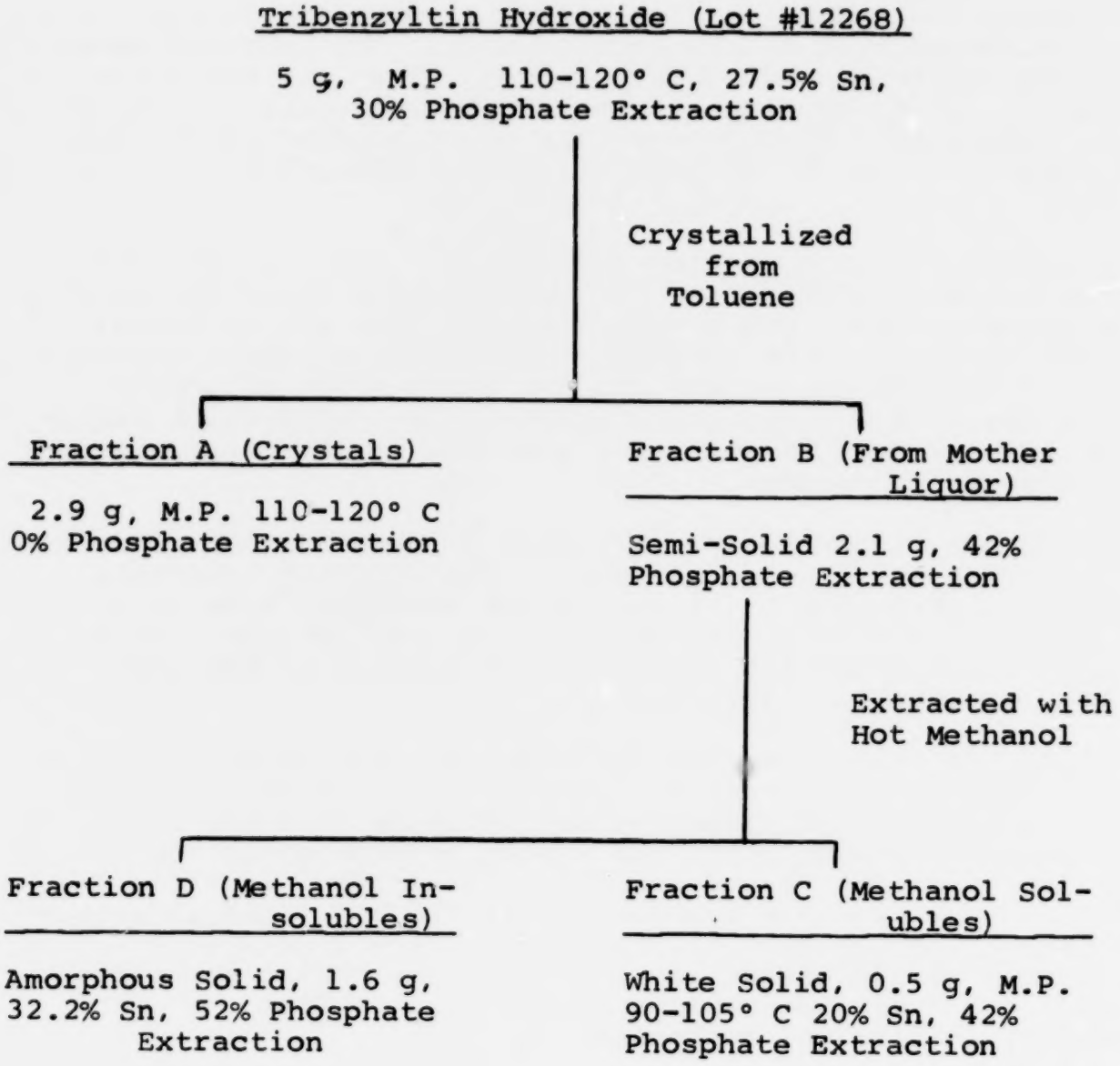
The mother liquor solids (Fraction B) were further purified by extraction with hot methanol. The methanol insoluble portion, (Fraction D) extracted 52% phosphate from pH 4.1 phosphate solution. The methanol soluble portion, (Fraction C) extracted 42% phosphate. A summary of the above data is given in Figure 2.

All of the fractions from the fractionation of tribenzyltin hydroxide were examined by infrared spectroscopy. The infrared spectrum of tribenzyltin hydroxide (Lot no. 12268), as previously mentioned, had a weak absorption in the OH region of 2.75-3.0μ and a moderate absorption at 7.4 and 9.05μ. One possible assignment for the 7.4μ band is a carbonate. Lohmann (11) reports a very strong band at 7.4μ for triethyltin carbonate. He also mentions that triethyltin oxide and hydroxide absorbs carbon dioxide from the air readily to form the carbonate.

Fraction A had an infrared spectrum different from that of tribenzyltin hydroxide (Lot #12268). The total OH absorption and the absorption at 9.05μ of fraction A were slightly stronger and the 7.4μ band was missing in fraction A.

The infrared spectrum of fraction B differed from fraction A by having a rather strong 7.4μ band and no absorption at 9.1μ. No assignment could be made for the 9.1μ band. Fraction B also had a weak 5.86μ band (not present in A) which is probably due to benzaldehyde.

FIGURE 2. FRACTIONATION OF TRIBENZYLTIN HYDROXIDE



Fraction C had more OH absorption than any of the other fractions. Fraction C also had the 7.4μ band, which is believed due to carbonate. It also had a trace of benzaldehyde. Upon rerunning the spectra of fraction C five weeks, later significant changes had occurred. Bands at 6.5μ and 7.05μ were present that were not present before. It is very likely that an ionized carboxyl group is responsible

for the new bands.

The infrared spectrum of fraction D has only moderate differences from the spectrum of fractions B & C. The 9.5μ and 7.4μ bands were about 50% stronger in fraction D than in either C or B.

Fraction D was separable into four spots by thin layer chromotography (TLC). The TLC plates were solvent developed with a 3:1 mixture of toluene and methanol. The spots were observed with ultraviolet light and color was developed with concentrated sulfuric acid spray. The R_f values were 0, 0.45, 0.60, 0.70. Additional experiments showed that the phosphate-active component was at R_f = 0 (original spot).

A toluene solution of D was shaken with aqueous phosphate to form organic-phosphate complex in the toluene phase. The resulting toluene solution loaded with phosphate was subjected to TLC.

Again four spots resulted (ultraviolet light identification) at the same R_f values as the solution of D alone. Only the spot at the origin, R_f = 0, showed phosphate activity on spraying with ammonium molybdate solution.

A preparative TLC was done on fraction D. The orgin spot was collected and analyzed by infrared spectroscopy. The infrared spectra was rather confusing. Part of the sample was benzaldehyde; part gave appreciable alphatic CH_2 absorption and there was a component which showed strong OH absorption. However, the OH absorption was stronger than anticipated for tribenzyltin hydroxide.

The above data indicated that the tribenzyltin hydroxide (Lot #12268) was of questionable composition. To clarify this point, an attempt was made to prepare some tribenzyltin hydroxide by contacting the corresponding chloride with sodium hydroxide. The procedure was as follows: 5 g of recrystallized tribenzyltin chloride (M.P. 135-142° C), Alpha Inorganics, was dissolved in 250 ml of toluene and contacted three times with 150 ml of aqueous 0.5M sodium hydroxide. The aqueous raffinate from the final contact gave a negative silver nitrate test for chloride. The toluene solution then was washed with distilled water until neutral, filtered through paper and placed in a refrigerator. After standing overnight, the solution was filtered yielding 3.5 g of clear square cyrstals (M.P. 119-124°). These crystals were similar in appearance to the crystals of fraction A in the "tribenzyltin hydroxide" separation

scheme. The crystals were redissolved in toluene and contacted with pH 4.1 phosphate solution. No extraction of phosphate was observed. The infrared spectrum of the crystals showed a very weak OH band and a strong 9.1μ band. The carbonate band, 7.4μ, was absent. The above data indicate we were unsuccessful in preparing the hydroxide. In fact, we probably made the oxide.

A similar experiment was run without attempting to isolate the tribenzyltin hydroxide, thus perhaps avoiding conversion to the oxide. The resultant toluene solution extracted 9.7% phosphate from a pH 4.1 solution. Although this is an increase in phosphate activity, it does not compare to the 30% phosphate activity with our original "tribenzyltin hydroxide" sample.

Tribenzyltin Acetate

The studies in "tribenzyltin hydroxide" indicated that there is some component other than the hydroxide which is doing the phosphate extraction. One possibility was tribenzyltin acetate. Therefore, a 4.74 g/l solution of tribenzyltin acetate (from Alpha Inorganics) in toluene was shaken in a separatory funnel for 2 minutes with aqueous phosphate solutions at pH 4.1, 7.0, and 8.3. The results are given in Table III.

TABLE III. EXTRACTION OF PHOSPHATE WITH TRIBENZYLTIN ACETATE

Volume Ratio Org/Aq	pH initial	pH final	[Phosphate] i., mg/l	[Phosphate] f., mg/l	% Phosphate Extracted
25/100	8.30	7.41	24.1	15.7	34.9
25/100	7.00	7.23	23.6	16.3	31.0
25/100	4.10	4.68	24.2	14.6	39.7

There was no extraction of chloride or sulfate by the tribenzyltin acetate. The experiment at pH 8.3 was repeated in order to check the validity of the phosphate results and also to check for bicarbonate extraction. (In the previous experiment, there was not enough sample to check for HCO_3^-

extraction.) Results of the repeat experiment were: 41.7% extraction of phosphate and 44.8% extraction of bicarbonate (from 262 mg/l to 146 mg/l HCO_3^-).

Extraction isotherm data were obtained on this commercial sample of tribenzyltin acetate to help clarify its activity. Separatory funnel extraction experiments were done as before, but only at pH 4. The resulting isotherm is shown in Figure 3. The shape of the isotherm indicated excellent extraction characteristics. Figure 4 is the isotherm data replotted and shows that the phosphate could be completely extracted if there are large amounts of active extractant present. Assuming that tribenzyltin acetate is the extractant, the isotherm data indicates only 4% of theoretical loading of phosphate is being achieved.

Infrared data indicate the sample is approximately 75% acetate. The shape of the isotherm, however, implies that an impurity rather than the acetate is actually doing the extraction. Additional work would be necessary to prove this conclusion. The above data on commercial tribenzyltin acetate indicates again, like with tribenzyltin hydroxide, that an impurity is responsible for the phosphate extraction. Therefore, some tribenzyltin acetate was prepared. The procedure was as follows: a sample of tribenzyltin chloride from K & K laboratories, M.P. 136-142° C (literature reports 142-144°), in toluene was shaken with 10% aqueous sodium acetate two times. The final aqueous raffinate gave a negative silver nitrate test for chloride. Based on chloride analysis, 94% conversion was achieved. After washing and filtering through paper, the toluene solution of tribenzyltin acetate was contacted with phosphate solutions at pH 8.0, 7.0, and 4.1 in the usual manner. Table IV gives the results of the phosphate extraction.

TABLE IV. EXTRACTION OF PHOSPHATE WITH LABORATORY PREPARED TRIBENZYLTIN ACETATE

Volume Ratio Org/Aq	pH initial	pH final	[Phosphate] i., mg/l	[Phosphate] f., mg/l	% Phosphate Extraction
25/100	8.05	7.32	23.0	21.4	10.8
25/100	7.00	7.18	23.6	20.4	13.5
25/100	4.10	5.20	24.2	19.1	21.1

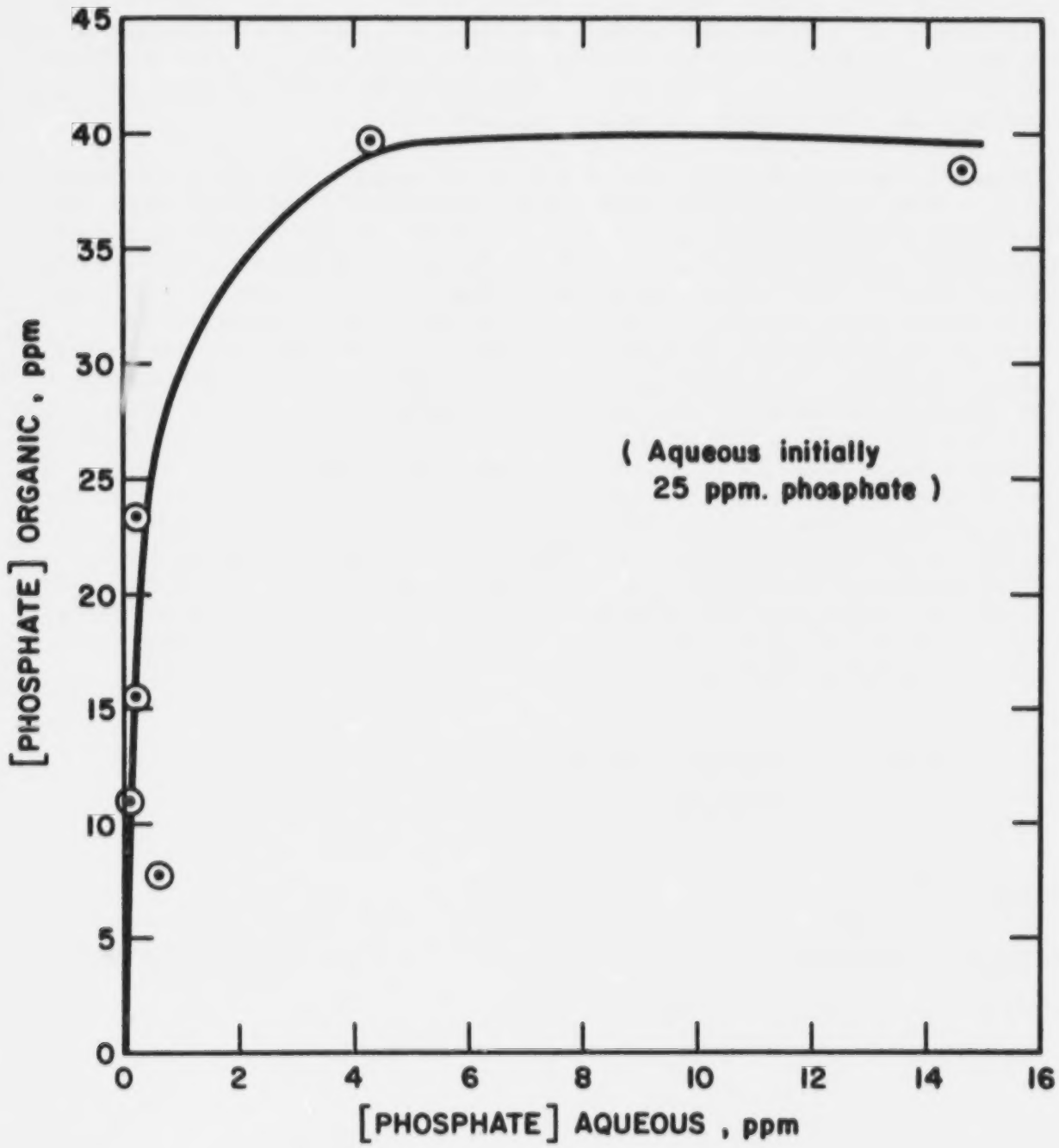


Figure 3. Phosphate Extraction Isotherm for Tribenzyltin Acetate

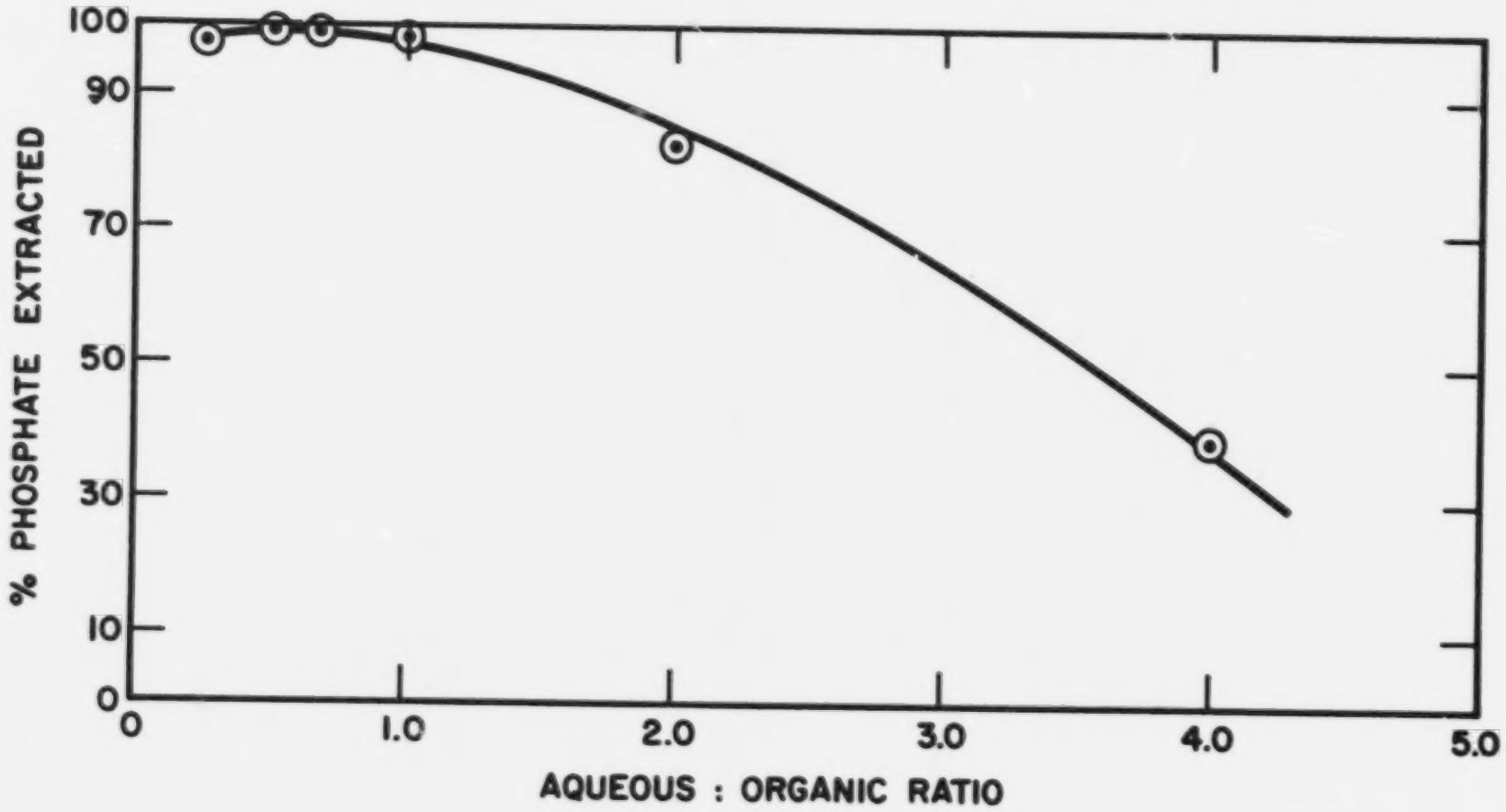


Figure 4. Extraction of Phosphate by Tribenzyltin Acetate

The data in Tables III and IV indicate the laboratory prepared tribenzyltin acetate has only about one half the phosphate extraction activity of the commercial sample. The lower phosphate activity again indicates that something in addition to the tribenzyltin acetate is extracting phosphate.

Tribenzyltin Carbonate

Another possible impurity in tribenzyltin hydroxide that might be the active ingredient is tribenzyltin carbonate. Tribenzyltin carbonate was prepared as follows: an 8.98 g/l solution of tribenzyltin chloride in toluene was shaken with an equal volume of 5% aqueous sodium carbonate three times. Final aqueous raffinate gave a negative silver nitrate test for chloride. The toluene solution was washed with distilled water until neutral. The resultant toluene solution was tested for phosphate extraction at pH 4.1 and 8.0 in the usual manner. Results are given in Table V.

TABLE V. EXTRACTION OF PHOSPHATE WITH TRIBENZYLTIN CARBONATE

Volume Ratio Org/Aq	pH initial	pH final	[Phosphate] i., mg/l	[Phosphate] f., mg/l	% Phosphate Extracted
25/100	8.05	8.20	23.0	23.4	0
25/100	4.10	6.72	24.2	22.7	6

The above phosphate extraction results are lower than expected. A portion of the toluene solution of tribenzyltin carbonate before extraction was evaporated to dryness in order to obtain a sample for infrared analysis. The infrared spectrum of the residue indicated no carbonate formation and looked like that of the starting material, tribenzyltin chloride. The original tribenzyltin carbonate sample showed a small amount (5-10%) of absorption at 7.4μ, which could be due to carbonate.

The residue sample which was analyzed by infrared, was redissolved in toluene and shaken with pH 4.1 phosphate solution. This time 22% phosphate was extracted as compared to

6% before evaporation and redissolving in toluene. The above data is somewhat confusing. Perhaps there was very little, if any, conversion to the carbonate while the sample was in solution. Upon removal of solvent there may have been more of the chloride converted to the carbonate by reaction with carbon dioxide in the air. Thus, the 5-10% of carbonate indicated by infrared may be responsible for the 22% extraction of phosphate. A pure sample of tribenzyltin carbonate would be needed to prove this theory.

Tributyltin Benzoate

Throughout the infrared examinations of "tribenzyltin hydroxide" fractions, ionized carboxyl and small amounts of benzaldehyde were evident. This leads to the belief that perhaps an organotin benzoate might be a phosphate extractant. A sample of tributyltin benzoate was obtained from Alpha Inorganics and tested for phosphate extraction at pH 8.0, 7.0, and 4.1. Results are given in Table VI.

TABLE VI. EXTRACTION OF PHOSPHATE WITH TRIBUTYLTIN BENZOATE

Volume Ratio Org/Aq	pH initial	pH final	Phosphate i., mg/l	Phosphate f., mg/l	% Phosphate Extracted
25/100	8.05	7.81	23.0	23.0	0
25/100	7.00	7.80	23.6	23.4	0
25/100	4.10	5.20	24.2	23.0	5.0

The results of Table VI indicate tributyltin benzoate probably is not our unknown phosphate extractant.

SUMMARY OF RESULTS WITH ORGANOTIN COMPOUNDS

A fraction from a commercial sample of tribenzyltin hydroxide selectively extracted 52% phosphate at pH 4.1 in the presence of chloride and sulfate. Although positive identification was never achieved the active ingredient might be tribenzyltin hydroxide, carbonate or a tribenzyltin carboxylic acid salt. A commercial sample of tribenzyltin

acetate was found to extract phosphate over a pH range of 4.1 to 8.0. Maximum extraction of 40% was achieved at pH 4.1. Extraction was selective over chloride and sulfate but not bicarbonate. Forty-five percent of bicarbonate was extracted. However in this case also, it appears that the extraction activity is due to a minor constituent.

The data are insufficient to tell if tribenzlytin carbonate extracts phosphate. A preparation containing 5-10% of tribenzyltin carbonate extracted 22% phosphate at pH 4.1. Tributyltin benzoate is ineffective for extracting phosphate.

MISCELLANEOUS ORGANOMETALLICS

A variety of organometallics were screened for extracting phosphate. The screening process was the same as with "tribenzyltin" compounds, i.e., contacting an organic solution of the organometallic with aqueous phosphate solutions at pH 8.3, 7.0, and 4.1. The compounds tested were triphenyltin hydroxide, tri-n-butyltin hydroxide, triphenylantimony hydroxide, triphenyllead hydroxide and triphenylarsenic hydroxide. Except for triphenyltin hydroxide, all of the above compounds were received as the chloride and were converted to the hydroxide by contact with aqueous sodium hydroxide. A summary of the results of these organometallics is given in Table VII.

The results of the triphenylantimony hydroxide and the triphenylarsenic hydroxide must be viewed with caution since precipitates formed during phosphate analyses. Arsenic is known to interfere with the phosphate analysis. In order to determine if the triphenylarsenic hydroxide contains analytical interferences, a 4.03 g/l toluene solution of triphenylarsenic hydroxide was contacted with an equal volume of 0.1 M bisulfate solution. The aqueous bisulfate raffinate solution was combined with an equal volume of 23.4 mg/l, pH 4.1 phosphate solution and analyzed for phosphate. The resultant analysis gave a value of 8.0 mg/l phosphate. Theoretically, 11.7 mg/l should have been obtained. Thus, the value was 32% low.

A similar test for analytical interferences was done with the triphenylantimony hydroxide. The test was: to an extraction raffinate, which analyzed 17.3 mg/l phosphate, was added an equal volume of 50 mg/l phosphate solution. The resultant solution analyzed 31.4 mg/l (theory is 33.6 mg/l) or 6.5% low. Thus, the results with triphenylantimony hydroxide may be fairly valid. However, caution should still be used when interpreting the triphenylantimony hydroxide

TABLE VII. EXTRACTION OF PHOSPHATE BY MISCELLANEOUS ORGANOMETALLICS

Compound	Org/Aq	pH initial	pH final	Phosphate i, mg/l	Phosphate f, mg/l	% Phosphate Extrd	Organic Solvent	Conc Org, mg/l
Triphenyltin hydroxide								
	1/2	8.31	8.58	24.1	23.4	2.9	Toluene	3860
	1/2	7.00	7.99	23.6	24.2	0		
	1/2	4.10	6.49	24.8	24.2	0		
Tri-n-butyltin hydroxide								
	1/4	8.31	8.69	24.1	23.8	0	Toluene	3240
	1/4	7.00	8.09	23.6	24.5	0		
	1/4	4.10	7.42	24.8	22.4	9.7		
Triphenylantimony hydroxide								
	1/4	8.31	8.65	24.1	16.3*	32.7	Benzene	4070
	1/4	7.00	8.20	23.6	15.7*	33.4		
	1/4	4.10	7.00	24.8	12.3*	50.6		
	1/4	4.10	7.08	24.8	17.3*	30.3		
Triphenyllead hydroxide								
	1/4	8.31	9.40	24.1	23.0	4	Chloro-	4840
	1/4	7.00	9.29	23.6	23.0	2.6	form	
	1/4	4.10	9.31	24.8	23.4	6.0		
Triphenylarsenic hydroxide								
	1/4	8.31	8.68	24.1	15.7*	34.8	Toluene	4030
	1/4	7.00	8.30	23.6	15.9*	32.7		
	1/4	4.10	5.23	24.8	15.4*	38		

* Precipitates formed during analysis for phosphate.

data. In view of the possible toxicity problems with antimony compounds we decided to concentrate our research on organotin compounds rather than antimony compounds.

EXTRACTION OF PHOSPHATE BY METAL SALTS OF DI-2-ETHYLHEXYL-PHOSPHORIC ACID (D2EHPA)

A literature survey (see Appendix) has revealed a wide variety of compounds, clays, humates, lipids, and proteins which appear to bind metal ions such as Cr^{+3}, Al^{+3} and Fe^{+3}. The above technique may be useful for selectively extracting phosphate. Al^{+3}, Fe^{+3} and Cr^{+3} metal salts of Di-2-ethylhexylphosphoric acid (D2EHPA) were chosen as possibilities for phosphate extraction. The equivalency ratios of metal to D2EHPA were varied in order to obtain the desired metal salt, namely $M(OH)_2O_2P(OR)_2$, where M is the metal ion, e.g., Fe^{+3} and R is $CH_2CH(C_2H_5)CH_2CH_2CH_2CH_3$. It was theorized that the hydroxyl group of this chemical species would exchange for H_2PO_4 or HPO_4.

Iron, Aluminum and Chromium Salts of D2EHPA

The general experimental procedure for preparing the iron salt of D2EHPA was as follows: A 0.01065N toluene solution of D2EHPA, aqueous $FeCl_3 \cdot 3H_2O$ and aqueous NaOH were shaken together in a separatory funnel for 2 minutes. The aqueous layer was drawn off and the pH was determined. The toluene phase was washed with distilled water until neutral.

The resultant toluene solution of iron salt of D2EHPA was contacted with phosphate solutions at pH 4.0, 7.0 and 8.3 in the same way as described earlier. The equivalency ratio of D2EHPA to Fe^{+3} (and the raffinate pH) were varied from 2:1 - 1:1.33 in order to give different complexing conditions. The resulting data indicated that very little, if any, phosphate was extracted by the iron salt of D2EHPA. The formation of fine precipitates complicated analyses in this portion of the study.

Aluminum and chromium salts of D2EHPA were prepared and tested in a manner similar to that used for the iron salt. Neither of these showed any significant activity in extracting phosphate.

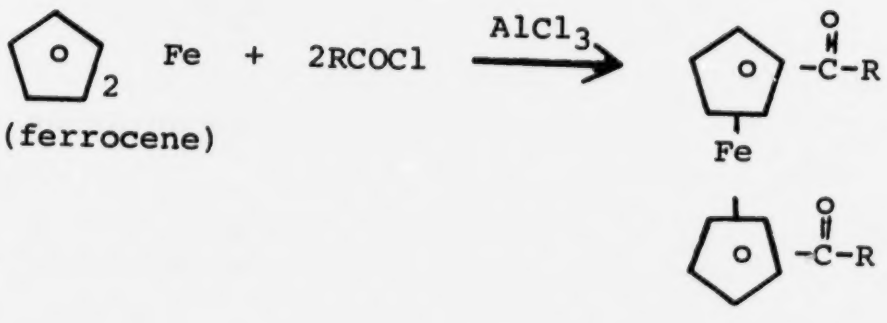
FERROCENIUM COMPOUNDS

It was postulated that ferrocenium compounds would extract phosphate. The extraction would be achieved by exchanging the anion of the ferrocenium compound for $H_2PO_4^-$, e.g.,

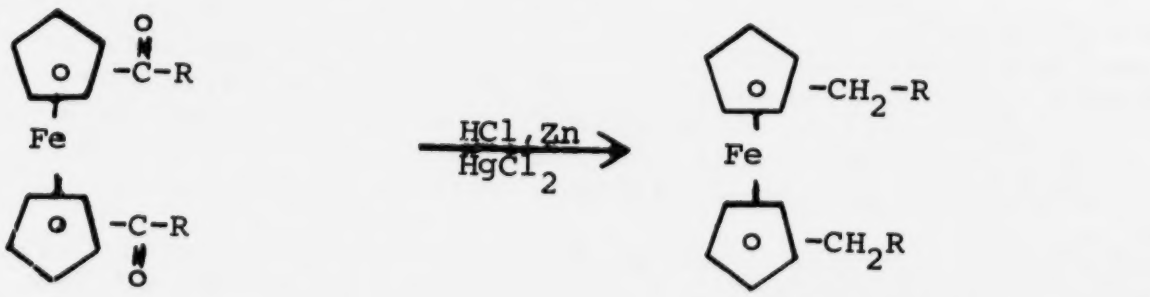
where A is an anion such as chloride or sulfate.

In order to achieve solubility in organic solvents it was necessary to prepare an alkylated ferrocenium compound. With the proper alkylated ferrocenium compound the normal liquid ion exchange process could be used.

The procedure of Vogel (12) was used for preparing the intermediate alkylated ferrocenes. The synthesis involves the Friedel-Crafts acylation with an acid chloride in presence of $AlCl_3$ followed by a Clemensen reduction of the acyl derivative.

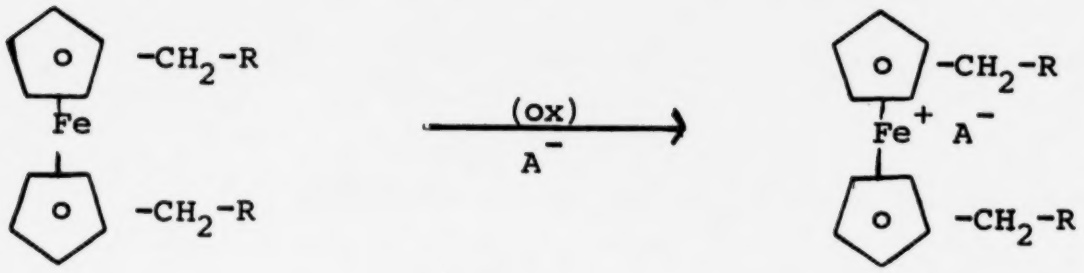


(ferrocene)



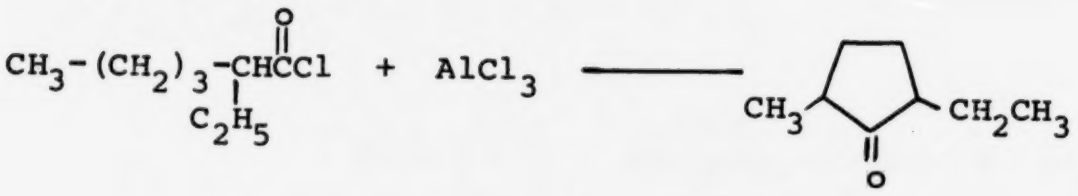
(alkylated ferrocene)

The alkylated ferrocene on oxidation would give the desired alkylated ferrocenium compound.



(alkylated ferrocenium compound)

The first choice for an alkylated ferrocene was 1,1'-di (2-ethylhexyl) ferrocene. Synthesis of this latter compound was unsuccessful due to an unexpected side reaction occurring during the Friedl-Crafts acylation. The side reaction was as follows:



2-methyl-5 ethyl cyclopentanone

This side reaction has been reported (13). The next choice was to synthesize 1,1'-didecylferrocene, which was prepared successfully.

The literature (14,15,16) reports ferrocene to be easily oxidized anodically or by a variety of chemical oxidants to the stable, blue ferrocenium cation $Fe(C_5H_5)_2^+$. Electrolytic oxidation of 1,1'-didecylferrocene was achieved in a $HClO_4$-95% ethanol solution. However, attempts to isolate the "ferrocenium" cation in toluene were unsuccessful.

The experiment procedure was as follows: A solution of 0.1g 1,1'-didecylferrocene and 1 g of 70% $HClO_4$ in 100 ml of 95% ethanol was placed in an electrolytic cell. The electrolytic cell consisted of a 250 ml beaker, a magnetic stirrer, a platinum gauze anode and a copper cathode. A potential of 4.1 volts was applied to the cell. The solution gradually changed from a yellow to a green to a blue-green color. When the blue-green color was achieved, the passage of current was stopped. (Further application of current results in a yellow solution, which according to infrared spectroscopy is a mixture of hydroxyl and carbonyl compounds.) Attempts to extract the blue "ferrocenium" cation from the

95% ethanol into toluene resulted in a yellow toluene solution. Infrared analysis of the yellow toluene solution indicates no "ferrocenium" ion and only evidence of both hydroxyl and carbonyl absorption. This data indicates the alkylated ferrocenium compound underwent further oxidation to oxygen-containing structures.

Chemical oxidation by CrO_3 was successful in achieving the blue ferrocenium ion. However, the blue alkylferrocenium ion was stable only for a short time. Oxidation was achieved as follows: A 7.5 ml of a 2%, wt/vol, solution of 1,1'-didecylferrocene in Skellysolve B was shaken for 15 minutes with 37.5 ml of a solution containing 0.284 g Cr_2O_3-50 g $HClO_4$ per liter. The aqueous phase was drawn off and the resultant blue organic phase was dried over Na_2SO_4. An infrared spectrum was run on the blue organic solution immediately. The infrared spectrum indicated ferrocenium ion to be present as evidenced by an absorption at 12.65μ (17). The blue organic solution of ferrocenium ion gradually turned yellow over a period of a few hours. Thus, it appears that alkylferrocenium ions are not as stable as ferrocenium ions.

Thus in summary, synthesis of 1,1'-didecylferrocene was achieved. Oxidation of 1,1'-didecylferrocene with CrO_3 resulted in the corresponding "ferrocenium" ion. However, this alkylferrocenium ion was not stable. Although unalkylated ferrocenium compounds are known to be stable, it appears our 1,1'-didecylferrocenium is not. Since alkylation is necessary to provide solubility in the organic solvents of the liquid ion exchange process, research on ferrocenium compounds was terminated.

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ADDENDUM - AMMONIA EXTRACTION

CHANGE IN SCOPE OF CONTRACT NO. 14-12-590

We propose that the scope of the contract be changed from phosphate extraction to ammonia extraction. The emphasis would be on the extraction of ammonia from waste water that has undergone treatment with lime. Thus, the objective would now be to determine the feasibility of liquid ion exchange for extracting ammonia from waste waters.

The research program would be concentrated on developing a liquid ion exchange reagent that selectively extracts ammonia at elevated pH. Immediate emphasis would be on screening organic complexes or organic salts of transition metals for this extraction. Such compounds have the potential for forming complexes with ammonia. For example, tridentate complexes of copper would have a coordination site available for complexing ammonia. Therefore, they could be the basis for a liquid ion exchange reagent that is selective for ammonia.

The experimental program would be similar to the one originally proposed for phosphate. A literature survey would be made for functionalities that have potential for complexing ammonia. Candidate compounds would be purchased or, if necessary, synthesized for testing.

Ammonia extraction screening tests would be performed in separatory funnels. Solutions of potential extractants in an organic solvent would be contacted with an aqueous solution which simulates effluent which has been treated with lime. Generally, this aqueous solution would contain 20 ppm of ammonia and appropriate inorganic salts and cover a range of pH. Analyses then would be applied to determine the extent of ammonia extraction and selectivity.

Extraction isotherms would be drawn for compounds that show promise. The data then would be evaluated to determine if extractions are satisfactory for further consideration. Satisfactory extraction would be generally viewed as attaining 1 ppm of ammonia in the effluent in several extraction stages.

Methods for regenerating extraction activity would be checked out on compounds that demonstrate satisfactory extraction of ammonia. This also would be carried out in separatory

funnels by treatment of the organic solutions that have been loaded with ammonia. Means for ultimate disposal of the ammonia would be considered in these experiments.

At this stage, the most promising compound would be checked out on secondary effluent from the Anoka, Minnesota municipal sewage plant.

Finally, this proposed program would be covered by the cost and contract period stated previously in contract no. 14-12-590. Also, the personnel involved would not change.

EXPERIMENTAL DETAILS

A literature survey was started for functionalities that have potential for extracting ammonia.

Simultaneously, experiments were begun to screen transition metal salts of organic acids for ammonia extraction. Copper salts were chosen as a starting point. Cupric ion is known to complex with ammonia in the following manner.

$$Cu(H_2O)_n^{++} + 4NH_3 \longrightarrow Cu(NH_3)_4^{++} + nH_2O$$

A similar reaction was visualized for the cupric salt of an organic acid, namely:

$$(RCO_2)_2Cu(H_2O)_n + nNH_3 \longrightarrow (RCO_2)Cu(NH_3)_n + nH_2O$$

The cupric salt of di-2-ethylhexyl phosphoric acid was prepared and tested for ammonia extraction. A solution of the cupric salt in toluene was shaken in a separatory funnel with aqueous ammonia. The aqueous solution contained: 19 mg/l NH_3, 50 mg/l Na^+, 20 mg/l K^+, 10 mg/l Mg^{++}, and 20 mg/l Ca^{++}. Extractions with three different aqueous solutions of pH 5.4, 9.5 and 11 were planned. Only the results at pH 5.4 are available. These show an extraction of 6% ammonia.

A cupric salt of napthenic acid also was prepared but not tested yet for ammonia extraction. Attempts to prepare a cupric salt of dioctadecyl phosphoric acid were unsuccessful.

In preparation for the ammonia extractions, analyses were set up for the various cations contained in the aqueous solutions. For ammonia, a colorimetric analysis with Nessler reagent was set up. Atomic absorption was employed for the other cations.

APPENDIX

LITERATURE SURVEY - PHOSPHATE EXTRACTANTS

As a base for future experimental work, a survey of the literature (CA, up to and including Vol 67) was made. All abstracts which contained material bearing on the extraction of phosphates were examined. Those deemed of interest are included in the attached summaries.

The following conclusions have been arrived at:

1) Organometallic compounds of Group IV A (Ge, Sn, Pb) and Group V A (As, Sb, Bi) appear to be of most immediate value. Some compounds in these two groups not only extract phosphates from water but also exhibit selectivity for PO_4^{-3} over SO_4^{-2}.

2) Werner complexes which are water insoluble should exhibit ion exchange capabilities. Selectivity of such compounds is unknown.

3) A wide variety of compounds, clays, humates, lipids, protein, appear to react with phosphates through a bound metal ion such as Ca^{+2}, Al^{+3}, Fe^{+3}, etc. It may be possible to use such a technique to selectively extract phosphates from sewage.

4) A number of other possibilities are evident in the abstracts but the above three areas appear to show the most promise.

I. METAL CONTAINING EXTRACTANTS

A. Organometallic Compounds

Bock and Burkhardt (I-1) reported the extraction of Cl^-, Br^-, I^-, PO_4^{-3}, AsO_4^{-3}, CrO_4^{-2}, VO_4^{-3}, and SeO_3^{-2} by $Ø_3SnOH$ in ØH. Sulfate and NO_3^- are not extracted.

$Ø_3PbOH$ in $CHCl_3$ was used (I-2) to extract Cl^-, Br^-, I^-, PO_4^{-3}, AsO_4^{-3}, SeO_3^{-2} and others from neutral or slightly acidic solutions.

Schweitzer, et al (I-3) used $Ø_3SnOH$, $Ø_3PbOH$, $Ø_3Sb(OH)_2$ and $Ø_3As(OH)_2$ to extract PO_4^{-3} and other ions from solution.

B. Werner Complexes

Furman and State (I-4) used $[Co(NH_3)_5NO_3](NO_3)_2$ as a precipitating agent for the phosphomolybdate ion to give $[Co(NH_3)_5NO_3]H_3PMo_{12}O_{41}$. (See also I-5.)

Wolf and Forberg studied the reactions of a Cr (III)-triethanolamine complex with a variety of anions, including PO_4^{-3}. (I-6)

A number of workers have studied the reactions of cobalt-ammonia complexes with a number of ions, including PO_4^{-3}. None were used in solvent extraction systems. (I-7, 8, 9, 10.)

C. Glass

Various types of glass strongly absorb PO_4^{-3} ions on their surfaces. Baier (I-11) reports that this absorption is caused by 1) hydrolysis of alkaline earth silicates, borates, etc. to give them the alkaline earth hydroxide which then reacts with the phosphate or 2) by precipitation of difficultly soluble phosphate (i.e., Li_3PO_4) on the surface. The absorbed PO_4^{-3} is not readily removed. (I-12)

D. Organic Compounds Containing Metals (not including organometallics) and Humates

Strong acid cation exchange resins loaded with trivalent metals react with PO_4^{-3} to form complexes. (I-13) Ti^{+3} appeared to form the strongest complex.

The ability of soil to function as an ion exchange resin for PO_4^{-3} is well documented. Chaminade (I-14) showed that when humus is dissolved out of the soil that the resultant material contains a large amount of PO_4^{-3}. We concluded that the PO_4^{-3} is not held by the organic portion of the humus but rather is bonded to Ca^{+2} ions which in turn are bonded to the humus.

Chaminade also showed (I-15) that when $Ca_3(PO_4)_2$ is precipitated in the presence of humates that $Ca_3(PO_4)_2$ is not formed but rather a Ca-humate-PO_4^{-3} complex.

A review (in Japanese) (I-16) discusses various properties of nitro-humic acids including its complex compounds with phosphates.

Roldan showed that the phosphate binding power of peat can be improved by treating the peat with $Ca(OH)_2$. (I-17)

Kaila in an extensive study (I-18) isolated the effects of various variables on the absorption of p by soil. He concluded that Al content was the most important but that Fe was also significant. Extractable Ca was not a significant variable.

Weir and Soper (I-19) made Fe^{+3} humates and found evidence that non-carboxylic hydroxyls were important in the binding of the Fe^{+3} to the humate.

II. CELLULOSIC MATERIALS

Veder and Pascha (II-1) studied the relative affinities of ions for a material known as ECTEOLA-cellulose. They found the order to be (descending affinity) $OH^- > HPO_4^{-2} > SO_4^{-2} > NO_3^- > Cl^-$.

Aminocellulose (2.5% N) was found (II-2) to give the following order of extractability: $OAc^- > NO_3^- > H_2PO_4^- > Cl^- > SO_4^{-2}$. The material was effective only in acidic solutions.

III. LIPIDS

Lipids recovered from rat livers were converted to either the Ca^{+2} or K^+ form. $CHCl_3$ solutions of the Ca^{+2} form extracted 70 times more PO_4^{-3} than the K lipids. The Ca^{+2} lipids gave increasing PO_4^{-3} extraction as the pH was increased from pH 5.8 to 8.3. (III-1)

Phospholipids were shown to extract PO_4^{-3} into $CHCl_3$ by Kiyasu (III-2) and that microbial cofactor increased the extraction.

IV. PROTEINS

In a study on the reaction of polyphosphates with proteins and RNA, El'piner, et. al. (IV-1) used the polyphosphate complex of toluidine blue. The pyrophosphate also complexed with trypsin, inalin and myosin.

Muhlrad, et. al. (IV-2) found that at 0° C, myofibrils took up "considerable" amounts of labelled P^{32} and that the P^{32} was found bound to the myosin and not to lipids. Denatured myofibrils failed to take up the label.

The reaction of ATP or $PO_4^{\equiv}$ with human serum, egg albumin, casein, globulin, myosin and muscle protein fractions was investigated by Drabikowski (IV-3). The proteins were coagulated either at pH 3.6 or 5.8 and denaturization did not affect the reaction. The effects of chemical modification of the proteins were also studied. (Deamination, acetylation and esterification.)

Rogeness, et.al. (IV-4) showed that PMCG (N-methyl-3-piperidinol cyclopentylphenylglycolate bonded to the phosphate groups in lecithin and also with PO_4^{-3}.

Kokochashvili, et.al. (IV-5) studied the extraction of P^{32} (PO_4^{-3}) with albumin and casein and found that the bound PO_4^{-3} may be readily stripped by NaOH.

Mulder, et.al. (IV-6) theorized that the casein-phosphate complex was actually calcium caseinate with adsorbed $Ca_3(PO_4)_2$.

The uptake of PO_4^{-3} on casein was found to be greater in the presence of Ca^{+2} than when no Ca^{+2} was present. (IV-7)

In an electrophoretic mobility experiment with RNase, a marked binding of PO_4^{-3} on the RNase was found. (IV-8)

Szorenyi (IV-9) also demonstrated the binding of PO_4^{-3} on myosin.

The reaction of salmine with PO_4^{-3} was studied by Callanan, et.al. (IV-10) and Ui, et.al. (IV-11).

Courtois, et.al. studied the precipitation of conamandin (sweet almond protein) with PO_4^{-3}. (IV-12)

V. ADSORPTION OF PO_4^{-3} ON CLAY

The adsorption and release of PO_4^{-3} by clays and soils has been extensively studied. The general consensus is that the PO_4^{-3} reacts with Al^{+3}, Fe^{+3}, Ca^{+2}, Mg^{+2} or K^{+} which occur on the surface of the particles. (V-1 to V-9)

VI. ELECTRON ACCEPTORS

Sukhorukov, et.al. (VI-1) studied the interaction of PO_4^{-3} and various phosphate containing molecules (AMP, ADP, ATP, etc.) and electron acceptors such as tetracyanoethylene, p-benzoquinone, methylene blue, ribofalvine, chloranil, etc.

VII. FOAM FRACTIONATION

R. B. Grieves, et.al.has studied the removal of PO_4^{-3} from solutions by foam fractionation with ethylhexadecyldimethyl-ammonium bromide. (VII-1 to VII-3)

VIII. MISCELLANEOUS

The extraction of phosphoric acid with alcohols and amines from wet acid production has been extensively studied. (VIII-1 to VIII-3) These extractants generally are used for concentrated or highly salted solutions.

The precipitation of various phosphates with both biological and non-biological bases has been studied (VIII-4). They appear to be effective only in acid systems, however.

Phenothiazine and imipramine based drugs (tranquilizer type) form precipitates with phosphates. (VIII-5 to VIII-6)

Phosphates have been determined by forming the molybdophosphate ion, making the salt with an organic base and extracting the compounds into a water immiscible solvent. (VIII-7 to VIII-10)

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6 Title: FEASIBILITY OF LIQUID ION EXCHANGE FOR EXTRACTING PHOSPHATE FROM WASTEWATER

10 Author(s): Ditsch, LeRoy, Swanson, Ronald, and Milun, Albert J.

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27 Abstract: A variety of organic compounds were screened for utility in extracting inorganic phosphate from water by the liquid ion exchange process.

Organometallic compounds, metal salts of di-2-ethylhexyl phosphoric acid and ferrocenium compounds were investigated. Only certain organometallics showed significant activity and this activity appeared to be concentrated in minor constituents present in the samples. More specifically, tribenzyltin compounds, possibly the hydroxide or its acid salts, were active in selectively extracting phosphate in the presence of chloride and sulfate.

(Milun - General Mills)

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